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A TECHNICAL METHOD OF USING THE MERCURY ARC TO OBTAIN DATA AT WAVE LENGTH 560 mμ IN THE SPECTROPHOTOMETRIC ANALYSIS OF SUGAR PRODUCTS [1]

By H. H. Peters [2] and F. P. Phelps

ABSTRACT

From the data on 40 representative cane sugar products it is shown that the specific absorptive index, $-\log \mathbf{t}$, of these products for wave length 560 mμ may be calculated with sufficient exactness for all ordinary purposes by deducting 48 per cent of the difference between the values of $-\log t_{546}$ and $-\log t_{578}$ from $-\log t_{546}$. This interpolation permits the use of the mercury vapor lamp with spectral filters as the source of light for making routine spectrophotometric measurements on technical sugar product, thereby making possible the use of the spectrophotometric method of determining the color of sugar products in many instances where an elaborate spectrophotometer is not available.

It has been shown elsewhere [3] that wave length $\lambda = 560$ mμ acquires a particular importance in the quantitative spectrophotometric analysis of the absorption and transmission spectrum of technical sugar products. Through a simple measurement of absorption or transmission at this wave length it is possible to arrive at a nearly correct estimate of color in relation to the effective quantity of coloring material per gram of saccharine dry substance.

Unfortunately no suitable monochromatic light source of wave length $\lambda = 560$ is known. At present the measurement of absorption or transmission of sugar solutions at this wave length involves the use of a spectrophotometer which in many cases is not available in industrial sugar laboratories. The primary purpose of this paper is to show that the specific absorptive index [4] ($-\log_{10}\mathbf{t}$) of sugar products for wave length 560 mμ may be obtained with sufficient accuracy by interpolation between the $-\log \mathbf{t}$ values for the two mercury wave lengths, 546 and 578 mμ. Figure 1 shows curves for $\mathbf{t}$, $-\log \mathbf{t}$, and Q from $\lambda = 436$ to $\lambda = 700$ mμ for colored sugar products containing unit quantity of coloring material of the various types. *A* is the curve for A sucrose; *6XZ* the curve for 6 samples of soft sugars from

[1] Presented in abstract at the meeting of the American Chemical Society at Baltimore, April, 1925.
[2] Deceased.
[3] B. S. Tech. Paper No. 338.
[4] For the precise definition of the terms and symbols used throughout this paper see footnote 3 above.

localities X and Z; *7XZ* the curve for 7 samples from localities X and Z, etc. *S* is the curve representing the $-\log T$ of a Stammer plate so reduced in thickness that its $-\log T$ at $\lambda = 560$ is 0.000485. It is seen that this curve does not match at all well with any of the types of sugar coloring matters.

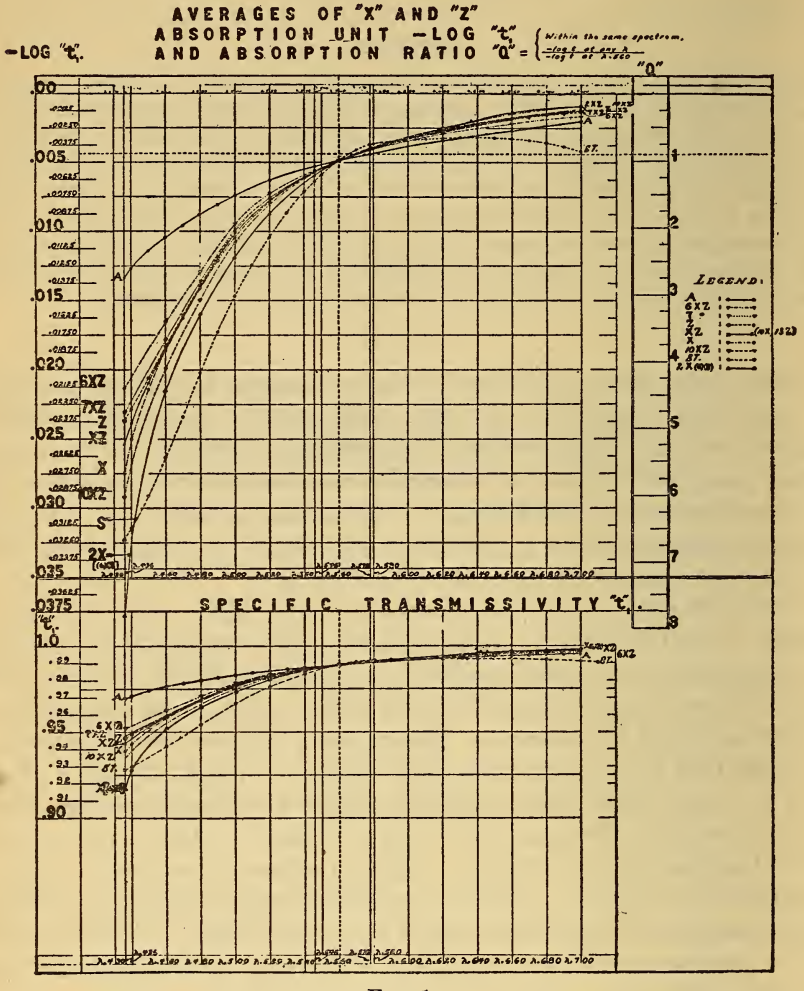

FIG. 1

It will be seen from these curves, which are representative of extreme types of coloring matter found in sugar products, that between the wave lengths 578 and 546 all the curves are very similar. They all are smooth curves with no sudden changes in direction, such, for instance, as occur in the case of dyes, and all slope in the same general direction; indeed, between these two wave lengths the curves are almost straight lines with differing slopes. The similarity is so great

that it would seem possible to obtain the value at 560 with sufficient accuracy for routine work by interpolating between the wave lengths 546 and 578. This would permit the mercury vapor lamp to be used as the light source in connection with one of the less expensive photometers and thereby simplify the problem of obtaining monochromatic light.

Priest and Peters [5] have used the mercury arc together with suitable spectral filters in connection with a Martens photometer for measuring the reflecting power of various substances. Bates [6] and Associates [7] first used the mercury arc together with spectral filters for the measurement of sugar colors in the spectrophotometric analysis of over 200 sugar products, of which approximately 150 were white sugars and the rest soft and raw sugars. The photometer used by the latter workers will be described in a subsequent paper. It was constructed from the well-known Stammer colorimeter by substituting for the Stammer color plates one of two interchangeable rapidly rotating sectored disks whose transmissions were 80 and 46 per cent, respectively. The column of filtrate was varied in length by the plunger until the light transmitted by the solution matched that transmitted by the sectored disk. This was done for each of three mercury wave lengths, the unwanted rays being in each case excluded by suitable color filters over the eyepiece. $-\text{Log } \mathbf{T}$ of the solution was then equal to $-\log T$ of the rotating sectored disk, from which $-\log \mathbf{t}$ could be calculated in the usual manner.

A Hesse-Ives tint photometer also has been used by substituting the mercury light and suitable spectral filters in place of the usual white light source and filters and using plane parallel glass cells of known thickness to hold the solution.

The specifications for spectral filters for use with the mercury arc may be obtained from the data presented by Gibson, Tyndall, and McNicholas in Bureau of Standards Technologic Paper No. 148 (1920), Ultra-violet and Visible Transmission of Various Colored Glasses; and by Gibson, "Spectral filters," J. Opt. Soc. Am. and Rev. Sci. Inst., **13**, p. 275; September, 1926.

As a result of the present investigation the following simple rule,[8] whose validity is predicated upon the prevalence of normal [9] absorption spectra, has been worked out for calculating the color value per gram of saccharine dry substance, or the colorimetric equivalent of $-\log \mathbf{t}$ at $\lambda = 560$, from the measured values at $\lambda = 578$ and $\lambda = 546$.

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[5] B. S. Tech. Paper No. 92.

[6] B. S. Sci. Paper No. 34.

[7] Comparative analysis of refined sugars, presented before Am. Chem. Soc., at Chicago, Ill., September, 1920. Abstract published in Internat. Sugar J., **22**, p. 654; 1920. Color values of high-grade sugars, presented before Am. Chem. Soc., at Birmingham, Ala., April, 1922. Abstract published in Internat. Sugar J., **24**, p. 296; 1922.

[8] See B. S. Tech. Paper No. 338, pp. 283–284.

[9] Absorption spectra of sugar products are considered normal if the absorption ratios, *Q*, of the samples in question are similar in magnitude to those here recorded. See p. 339.

Rule: (*a*) Calculate the difference, D (see Table 1, column 6), between $-\log \mathbf{t}$ at $\lambda=546$ and $-\log \mathbf{t}$ at $\lambda=578$.

(*b*) Subtract 48 per cent of the difference, D, so found from $-\log \mathbf{t}$ at $\lambda=546$. This gives within the experimental error the value for $-\log \mathbf{t}$ at $\lambda=560$ (Table 1, column 9).

(*c*) Convert [10] the $-\log \mathbf{t}$ at $\lambda=560$ into n color units or n units of coloring matter per gram of saccharine dry substance by means of the equation

$$n=\frac{-\log \mathbf{t}_{560}}{0.00485}$$

The validity of the above rule has been investigated only for concentrated transparent asbestos filtrates, prepared as recommended in Bureau of Standards Technologic Paper No. 338, and not for other solutions.

This rule has been found to hold for practically all of more than 300 spectra. Only 40 of these are presented here and they were selected as representative of typical absorption spectra of cane-sugar products of well-known color characteristics.

Whether the same method of conversion may also be applied safely in the case of beet-sugar products is a matter of conjecture for the reason that not many beet-sugar products were investigated. In the few instances for which it was tested it was found to hold. (See Table 3.)

I. ABSORPTION SPECTRA OF SUGAR PRODUCTS (TABLE 1)

Sections I and II of the table comprise so-called soft sugars as manufactured by two leading refineries which are designated X and Z. Section III consists of three groups of samples from consecutive stations in the refinery. Group III (1) consists of 9 sirups; Group III (2), 4 magmas; and Group III (3), 4 granulated sugars. The products to and from the "A," "B," and "C" pans are identified in the table by the letters (*a* to *d*). (*a*) designates the panfeed, a sirup to be boiled into the magma (*b*); the finished "strike" from this boiling goes to the centrifugals and is there separated into the run-off (*c*) and the granulated sugar (*d*). A run-off (*R. O.*) of a strike of an "A" pan becomes a panfeed (P. F.) to a "B" pan, and so on, the nonsugars and color increasing continuously from the "A" pan to the last run-off or tail-end (5*c*).

The specific absorptive indices, $-\log \mathbf{t}$, at $\lambda=436$, 546, 578, and 560 mμ of the 40 representative cane sugar products are presented in Table 1, columns 2, 3, 4, and 5. These $-\log \mathbf{t}$'s were measured on a precision spectrophotometer of the Nutting type made by Adam

[10] B. S. Tech. Paper No. 338, p. 267.

Hilger, the light source being a white-lined box (see Bureau of Standards Technologic Paper No. 338, p. 282) instead of the usual light source supplied by the makers.

The differences between the values of $-\log \mathbf{t}$ at 546 and at 578 (D) and between those at 546 and 560 (D_1) are shown in columns 6 and 7. The ratio, $\frac{D_1 \times 100}{D}$ for each sample; that is, the percentage of D which must be deducted from $-\log \mathbf{t}_{546}$ to give the measured value of $-\log \mathbf{t}$ at 560 is given in column 8. When it is considered that relatively large differences in the values in column 8 produce only small differences in the calculated $-\log \mathbf{t}$ values, it will be seen that the values in column 8 are all so nearly the same that the average value of 48 per cent is sufficiently accurate for use in commercial analyses. That this is true may readily be seen by comparing the measured values of $-\log \mathbf{t}_{560}$ in column 5 with the values in column 9, which were calculated from columns 3 and 4, using the factor of 48 per cent. The agreement is further brought out by comparing columns 10 and 11 wherein the $-\log \mathbf{t}$ values have been converted into units of coloring matter per gram of saccharine dry substance. Columns 12 and 13 give the differences between columns 10 and 11. It will be seen from column 13 that the difference seldom exceeds 1 per cent, which is considered to be within the experimental error of the measurements.

The calculation on the basis of 48 per cent is therefore sufficiently exact for all normal types of technical cane sugar products.

The absorption ratios, $Q = \frac{-\log \mathbf{t}_\lambda}{-\log \mathbf{t}_{\lambda=560}}$, for $\lambda = 436$, 546, and 578, are given in columns 14, 15, and 16 as an indication of the particular individual type of coloring matter in each sample. The Q ratio for 436 is of the greatest interest for this purpose. That for the other end of the spectrum, about 700 mμ, is next in importance, but, of course, is not obtainable with the mercury light.

Among the Q ratios at 436, soft sugar No. 6X stands out as a rather extreme limit. The Q ratios for all the others are normal in that they are of about the magnitude frequently occurring for each particular grade of product.

The rule given above has been tested and found valid for many other products ranging from white sugar to molasses. Table 2 shows some of these results.

TABLE 1.—*Absorption spectra of sugar products*

I. SOFT SUGARS OF LOCALITY X

Name or designation of product	−Log t (observed)				Difference		$\frac{D_1 \times 100}{D}$	−Log t calculated on the basis $\frac{D_1 \times 100}{D} = 48$	Units of coloring matter per gram of saccharine dry substance		Difference—		The ratio $Q = \frac{-\log t}{-\log t_{560}}$		
					D	D_1					Between columns 10 and 11; units of coloring matter	Between columns 5 and 9 and 10 and 11 expressed in per cent			
	λ=435	λ=546	λ=578	λ=560	λ=546 to λ=578	λ=546 to λ=560			Observed	Calculated			λ=436	λ=546	λ=578
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
							Per cent								
6X	1.040	0.1435	0.0926	0.1200	0.0509	0.0235	46.2	0.1191	24.74	24.56	−0.18	−0.75	8.67	1.20	0.77
7X	1.051	.2013	.1419	.1750	.0594	.0263	44.3	.1728	36.08	35.84	−.24	−1.3	6.01	1.15	.81
8X	1.4657	.2576	.1800	.2120	.0776	.0456	58.8	.2204	43.71	45.44	+1.73	+4.0	6.91	1.22	.85
9X	1.860	.3929	.2731	.3400	.1198	.0529	44.2	.3354	70.10	69.16	−.94	−1.3	5.47	1.16	.80
10X	2.099	.4266	.2932	.364	.1334	.0626	46.9	.3626	75.05	74.76	−.29	−.4	5.77	1.17	.81
11X	3.270	.7799	.5716	.681	.2083	.0989	47.5	.6799	140.4	140.2	−.2	−.2	4.80	1.15	.84
12X	4.146	.9536	.6856	.825	.2680	.1286	48.0	.825	170.1	170.1	0	0	5.03	1.16	.83
13X	4.040	.9032	.6571	.781	.2461	.1222	49.7	.7851	161.0	161.9	+.9	+.5	5.17	1.16	.84
14X	5.334	1.3372	.9939	1.18	.3433	.1572	45.8	1.1724	243.3	241.7	−1.6	−.6	4.52	1.13	.84
15X	6.973	1.878	1.400	1.646	.4780	.2320	48.5	1.6486	339.4	339.9	+.5	+.2	4.24	1.14	.85
II. SOFT SUGARS OF LOCALITY Z															
2Z	0.05776	0.01680	0.01223	0.01450	0.00457	0.00230	50.3	0.01461	2.99	3.01	+0.02	+0.76	3.98	1.16	0.84
3Z	.12463	.03501	.02429	.03000	.01072	.00501	46.7	.02986	6.19	6.16	−.03	−.47	4.15	1.17	.81
4Z	.20628	.05425	.03833	.04700	.01592	.00725	45.5	.04661	9.69	9.61	−.08	−.83	4.39	1.15	.82
6Z	.39762	.08406	.05742	.0715	.02664	.01256	47.1	.07127	14.74	14.70	−.04	−.32	5.56	1.18	.80
7Z	.73187	.15639	.10480	.13100	.05159	.02539	49.2	.13163	27.01	27.14	+.13	+.48	5.59	1.19	.80
8Z	1.1711	.27680	.19409	.2370	.08271	.03980	48.1	.2371	48.87	48.89	+.02	+.04	4.94	1.17	.82
9Z	1.3038	.26642	.18715	.2270	.07927	.03942	49.7	.22837	46.81	47.09	+.28	+.60	5.74	1.17	.82
10Z	1.8571	.38497	.27680	.3335	.10817	.05147	47.6	.33305	68.76	68.67	−.09	−.13	5.57	1.15	.83
11Z	3.1688	.76217	.54536	.6560	.21681	.10617	49.0	.65810	135.3	135.7	+.4	+.32	4.83	1.16	.83
12Z	3.7342	.86256	.64833	.7510	.21423	.11156	52.1	.75973	154.8	156.6	+1.8	+1.16	4.97	1.15	.86
13Z	5.8211	1.2456	.93624	1.090	.30936	.15560	50.3	1.0971	224.7	226.2	+1.5	+.65	5.34	1.14	.86
14Z	7.619	2.0934	1.5616	1.850	.5318	.2434	45.8	1.8381	381.5	379.0	−2.5	−.64	4.12	1.13	.84
15Z	14.7244	3.8908	2.9165	3.400	.9743	.4908	50.4	3.4231	701.0	705.8	+4.8	+.68	4.33	1.14	.86

III. PANFEEDS (P. F.), MAGMAS (M.), RUN-OFFS (R. O.), AND GRANULATED SUGARS (G. S.) FROM A REFINERY

III. (1) SIRUPS (PANFEEDS AND RUN-OFFS)

1(*a*). P. F. to "A" pan	0.03939	0.00811	0.00547	0.00690	0.00264	0.00121	45.8	0.00684	1.42	1.41	−0.01	−0.87	5.71	1.18	0.79
1(*c*). R. O. from "A" pan	.13422	.02910	.02081	.02485	.00829	.00425	51.3	.02512	5.12	5.18	+.06	+1.09	5.40	1.17	.84
2. "A" pan liquor	.09816	.02098	.01550	.01830	.00548	.00268	48.9	.01835	3.77	3.78	+.01	+.27	5.36	1.15	.85
3(*a*). No. 2 P. F. to "B" pan	.04178	.00701	.00513	.00615	.00188	.00086	45.7	.00611	1.27	1.26	−.01	−.65	6.79	1.14	.83
3(*c*). R. O. from "B" pan	.37089	.08137	.06094	.07150	.02043	.00987	48.3	.07157	14.74	14.76	+.02	+.10	5.19	1.14	.83
4(*a*). "B" P. F. to "C" pan	.37020	.10011	.07643	.08900	.02368	.01111	46.9	.08874	18.35	18.30	−.05	−.29	4.16	1.12	.86
4(*c*). R. O. from "C"	.80362	.21765	.14861	.18600	.06904	.03165	45.8	.18451	38.35	38.04	−.31	−.80	4.32	1.17	.80
5(*a*). No. 4 P. F. (tailend)	2.2015	.32622	.22825	.27700	.09797	.04922	50.2	.27919	57.11	57.57	+.46	+.79	7.95	1.18	.82
5(*c*). R. O. from tailend	4.3066	.69959	.45556	.5780	.24403	.12159	49.8	.58246	119.2	120.1	+.9	+.77	7.45	1.21	.79

III. (2) MAGMAS

1(*b*). "A" pan	0.07222	0.01893	0.01456	0.01680	0.00437	0.00213	48.7	0.01683	3.47	3.46	−0.01	+0.18	4.30	1.13	0.87
3(*b*). "B" pan	.14846	.03918	.02799	.03400	.01119	.00518	46.3	.03381	7.01	6.97	−.04	−.56	4.37	1.15	.82
4(*b*). "C" pan	.41955	.10840	.07963	.09500	.02877	.01340	46.6	.09459	19.59	19.50	−.09	−.43	4.42	1.14	.84
5(*b*). Tailend	2.1575	.30714	.21548	.26150	.09166	.04564	49.8	.26314	53.92	54.26	+.34	+.63	8.25	1.17	.82

III. (3) GRANULATED SUGARS

1(*d*). From "A" pan	0.01619	0.00641	0.00529	0.00587	0.00112	0.00054	48.2	0.00587	1.21	1.21	0	0	2.76	1.09	0.90
3(*d*). From "B" pan	.02269	.00779	.00643	.00715	.00136	.00064	47.1	.00714	1.47	1.47	0	−.14	3.17	1.09	.90
4(*d*). From "C" pan	.03741	.01081	.00808	.00955	.00273	.00126	46.2	.00950	1.97	1.96	−.01	−.52	3.92	1.13	.85
5(*d*). From tailend	.05832	.01419	.01083	.01265	.00336	.00154	45.8	.01258	2.61	2.59	−.02	−.55	4.61	1.12	.86

TABLE 2

	−Log t at 560	
	Observed	Calculated
Cane molasses from a refinery (1926)	20.26	20.31
Cane molasses from a plantation (1920)	11.73	11.75
Java sugar (raw) (1926)	1.49	1.48
Stammer's ulmin solution (diluted)	.378	.379
Caramel (J. S., 1923)	1.517	1.540
Caramel (B_2, 1923)	1.52	1.52
Stammer color plate ($-\log T_{560}$)	.150	.160

The rule apparently holds for many caramelization products and coloring matters produced in part at least by overheating near the steam coils in vacuum pans, etc.

Table 3 gives some data on beet molasses and beet nonsugar. This nonsugar is the desugarized residue of beet molasses, obtained by the barium saccharate process.

TABLE 3.—*The specific absorptive index of beet molasses and beet nonsugar*

λ	−Log t of—		"Q" absorption ration of—	
	Beet molasses	Beet nonsugar	Beet molasses	Beet nonsugar
660	0.870	4.35	0.041	0.33
620	1.29	6.97	.61	.53
580	1.77	10.47	.83	.80
578	1.80	10.70	.85	.82
560	2.125	13.12	1.00	1.00
546	2.40	15.40	1.13	1.17
540	2.52	16.52	1.19	1.26
500	3.55	25.68	1.67	2.00
460	5.56	44.59	2.62	3.40
435	8.48	61.15	3.99	4.66

From the data in Table 3 the values for beet molasses are $-\log t_{560}=\begin{cases}2.112 \text{ (calculated)}\\2.125 \text{ (observed)}\end{cases}$ and for the beet nonsugar $\log t_{560}=\begin{cases}13.14 \text{ (calculated)}.\\13.12 \text{ (observed)}.\end{cases}$

In the case of these beet sugar products also the rule is seen to hold.

SUMMARY

A rule has been developed for calculating the specific absorptive index ($-\log t$) of sugar products at wave length $\lambda=560$ mμ from the values of $-\log t$ measured at two of the wave lengths obtainable from the mercury vapor lamp. The rule has been tested for a large number of cane-sugar products, including refined sugars, raws, molasses, various intermediate refinery products (panfeeds, run-offs, magmas, etc.), caramelization products, and a few beet sugar products. In practically every instance it was found to hold, since the calculated value seldom differed by more than 1 per cent from the value obtained by actual measurement at $\lambda=560$ mμ by means of a spectrophotometer.

WASHINGTON, August 3, 1928.